



Micro determination of palladium (II) with Reagent (Antipyriyl azo 1-Nitroso-2-naphthol as a chelating Reagent by spectrophotometric methods

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Abstract:

A new, simple, sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of palladium (II). The method is based on the formation of a 1:1 complex with 3-(4'- antipyriyl azo) 1- nitroso-2-naphthol (APANN) as a new reagent is developed. The complex has a maximum absorption at 436.5 nm and ϵ_{\max} of $0.19 \times 10^5 \text{ L. mol}^{-1} \cdot \text{cm}^{-1}$. A linear correlation (0.1–2.0 $\mu\text{g. ml}^{-1}$) was found between absorbance at λ_{\max} and concentration.

Key Word: palladium (II) determination, Azo dyes, pyrazolen azo, spectrophotometric methods.

Introduction:

Azo compounds containing a heterocyclic moiety and their metal complexes play an important role in many practical applications for molecular memory storages, nonlinear optical elements, and printing system⁽¹⁻³⁾. They consist of N=N unit as a chromophore in their molecular structure. There is a great environmental concern about the fate of these dyes, where large amounts of dyes enter the wastewater streams during operation⁽⁴⁾. Some azo dyes are also used in biological systems where some can be used as inhibitors of tumor-growth^(5,6)

Antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one), its

derivatives and complexes with alkaline-earth, transition- and rare-earth metals are of considerable importance because of their potentially beneficial medicinal applications⁽⁷⁾.

At present, several techniques such as Reversed-Phase liquid chromatographic⁽⁸⁾, X-ray with differential thermal analysis⁽⁹⁾ and Flow injection⁽¹⁰⁾, show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis. In this study, we wish to report this reagent as a selective reagent in spectrophotometric determination of micro amounts of palladium (II).

Experimental:

I/ Synthesis of the azo compound (APANN)

The reagent was prepared by coupling 1-nitroso-2-naphthol with diazotate 4-amino antipyrine in

alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g of 4-amino antipyrine in 10 mL of ethanol and concentrated hydrochloric acid with 8 mL of distilled water and adding sodium nitrite solution drop wise at (0-5 C⁰). 1.1 g of 1-nitroso-2-naphthol was dissolved in 20 mL of ethanol and 26 mL of 4.0 M from sodium hydroxide were added at (0-5 C⁰). The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol⁽¹¹⁾.

Preparation of palladium(II)complex

The complex was prepared by direct reaction between palladium chloride and the appropriate ligand (APANN) in 1:1 mole ratio, using aqueous ethanol as solvent. The formed precipitate was filtered off, washed with warm water, then dried in a vacuum desiccator.

Apparatus

Spectrophotometric measurement were made with Shimadzu UV-visible-1650 PC double beam spectrophotometer using 1.00 cm glass cells. Vibrational spectra were recorded on Test scan Shimadzu FT.IR 8000 series. Measurements of pH were made using an , pH7110, pH-meter equipped with a glass-saturated calomel combined electrode. Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus. Conductivity was measured in DMSO, DMF and ethanol solution with an Mi 170 Bench Meter. Elemental analysis (C.H.N) were carried out with a EuroEA Elemental Analyser.

Reagents

All chemicals used were of analytical grades

Palladium (II) stock solution (1000 $\mu\text{g} \cdot \text{ml}^{-1}$)

Dissolve 0.8331 g of PdCl₂ (99%, Riedel-Dehaeng Seelz-Hannover) in 1 ml of 1M HCl and dilution the volume to 500 ml with distilled water. Working standard Pd (II) solutions were prepared by dilution of the appropriate volume of standard Pd (II) 1000 $\mu\text{g} \cdot \text{ml}^{-1}$ solution with distilled water.

3 -(4'- Antipyryl azo)1-Nitroso-2-naphthol (1 mM)

0.1937 g of reagent was dissolved in 500 ml of ethanol .

Foreign ion solutions (10 $\mu\text{g} \cdot \text{ml}^{-1}$)

All the solutions were prepared by dissolving an appropriate amount of the compound in distilled water in a volumetric flask.

General Procedure

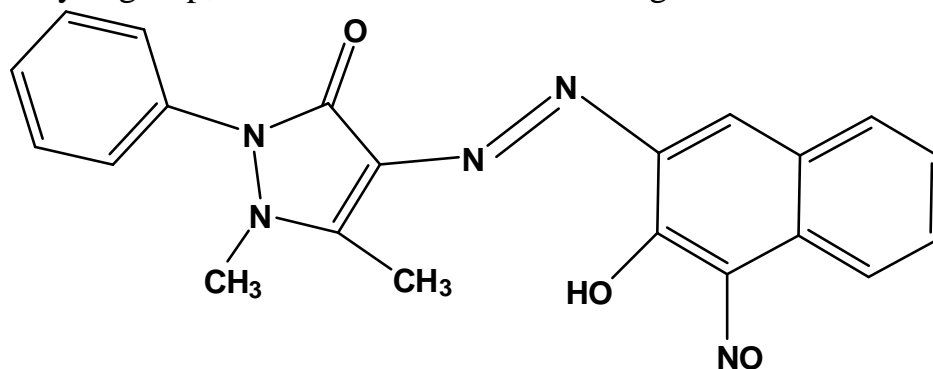
An aliquot of sample containing 1-30 μg of Pd(II) was transfer into a series of 10 mL standard flask. 2.5 mL of 1 Mm of APANN was added and pH was adjusted to 6.5. The complex formed were solubilized in water and diluted up to 10 mL in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition.

Results and Discussion

Properties of (APANN) and its metal chelate

APANN is a tridentate with coordination of azo group nitrogen, hydroxyl group

and carbonyl group; it has the following structure Schem.1:



Schem.1. structure of APANN

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. APANN and its metal chelates can be easily solubilized in an aqueous solution

.Elemental analyses were carried out on the resulting compound (C% calc. 65.11; found 64.46, H% calc.4.42; found 4.15, N% calc.18.08; found 17.99)⁽¹¹⁾. (m.p) 202 C⁰

Spectra

The result of this work indicated that the reaction of Pd (II) with APANN at pH yield highly soluble product which can be

utilized as a suitable assay procedure for Pd (II). This product has a maximum absorption at 436.5 nm Fig. 2 was adopted in all subsequent experiments.

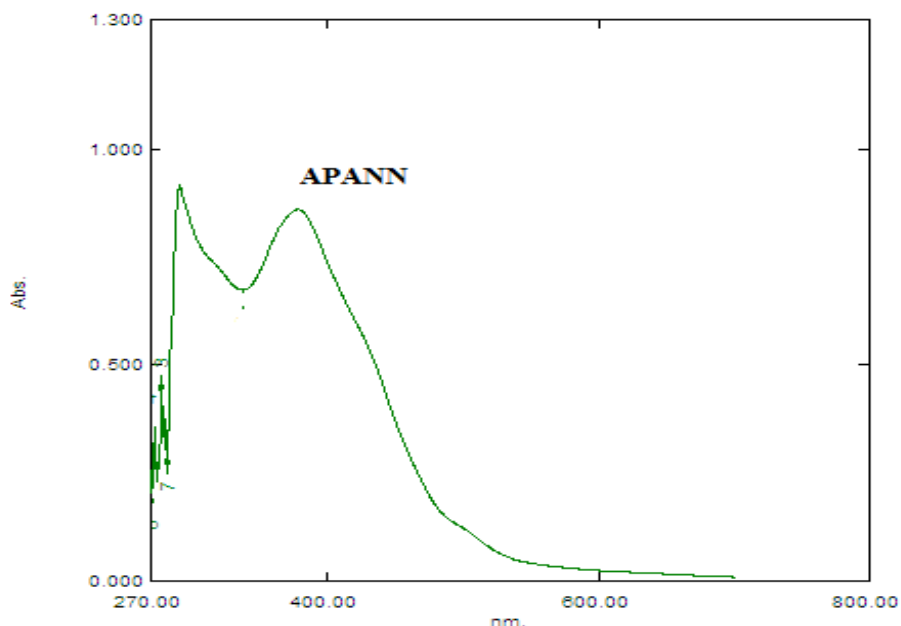


Fig.1 : Absorption spectra of a reagent against ethanol as blank.

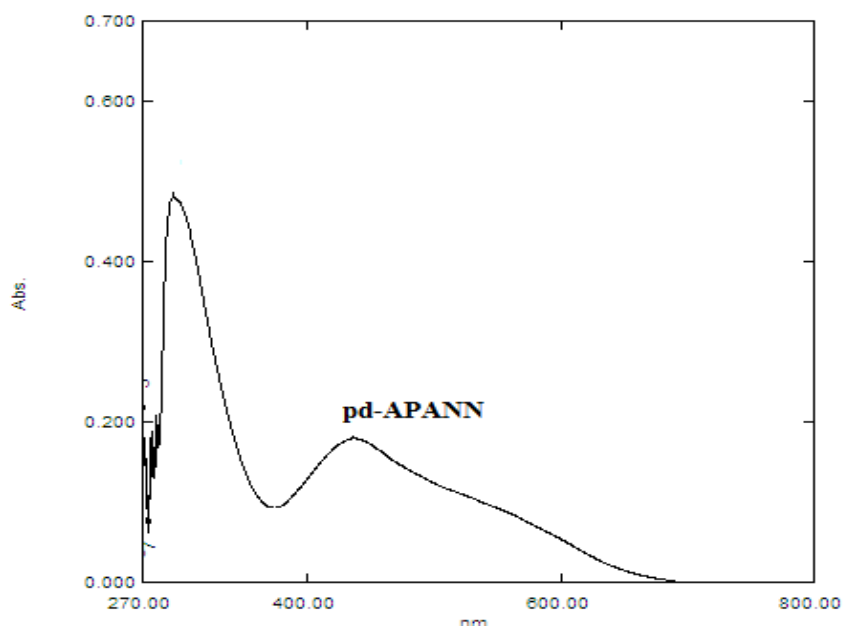


Fig. 2 Absorption spectra of [Pd (II) + APANN] treated as described under procedure and against a reagent blank.

The result of this investigation indicated that the reaction of Pd(II) with -(4'-anti pyriyl azo) 1- nitroso-2-naphthol yield highly soluble coloured complex which can be utilized as a suitable assay procedure for determination of Pd(II)). This coloured complex have maximum absorption at 436.5 nm for Pd(II), the blank at this wavelength shows zero absorbance (Fig. 2). The effect of various parameters on the absorption

intensity of the formed products was studied and the reaction condition were optimized. The bands appearing in the range of 270-373 nm are attributed to $\pi \rightarrow \pi^*$ transition. The other band observed in the region of 436.5 nm for Pd(II) is attributed to $n \rightarrow \pi^*$ electronic transition. that is in accordance with octahedral geometry of Palladium metal ion^(12,13).

Effect of pH

The pH of metal complex solutions was adjusted using dilute solutions (0.02M) NaOH and (0.02 M) HCl, and the effect on

absorbance was studied in Fig. 3. The absorbance of the complex was maximum and constant in the pH range given in Table.1.

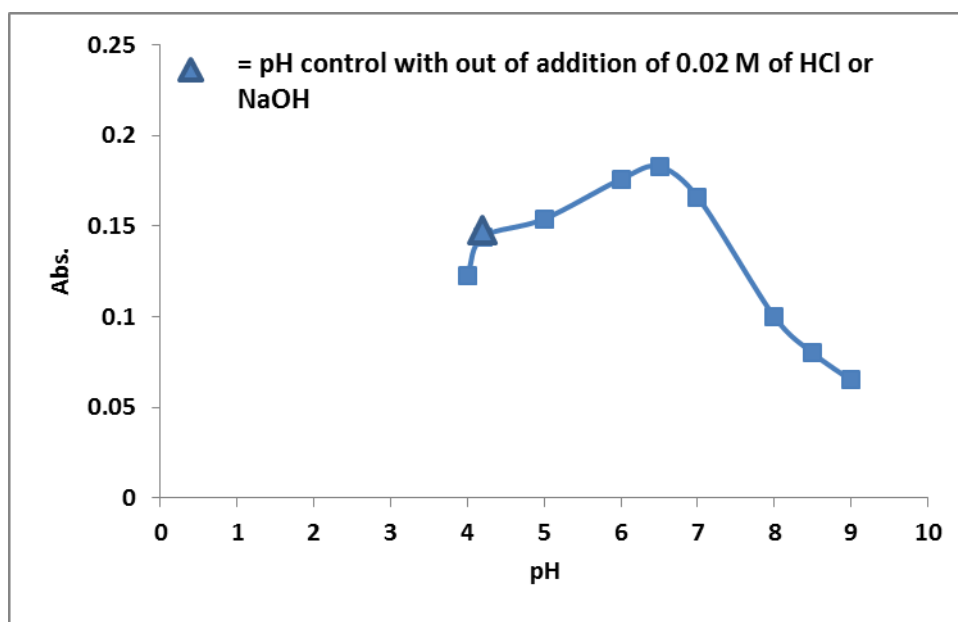


Fig.3. :- Effect of PH

Table.1 :- Analytical characteristics of Pd (II) – complex.

Characteristic	Pd (II) – complex
Absorption maximum for reagent (nm)	378
Absorption maximum for Pd(II)-complex (nm)	436.5
Beer's law range (ppm)	(0.1– 2.2)
pH range	(6 – 7)
Sandell's sensitivity $\mu\text{g} \cdot \text{cm}^{-2}$	0.0056
Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	0.19×10^5
Melting point for reagent	(200 – 202) $^{\circ}\text{C}$
Melting point for Pd (II) – complex	(277 - 279) $^{\circ}\text{C}$

Effect of (APANN) concentration

When various concentrations of of 3 –(4'- antipyriyl azo) 1-nitroso-2-naphthol was added to a fixed concentration of Pd(II), 2.5 mL of 1 mM (APANN) solution was sufficient to develop the colour to its full intensity and gave minimum

blank value, above 2.5 mL, the absorbance of the blank value was increased causing a decrease in the absorbance of the sample. Therefore, 2.5 mL of 1 mM of 3–(4'- antipyriyl azo) 1-nitroso-2-naphthol was used in all subsequent experiments (Fig. 4).

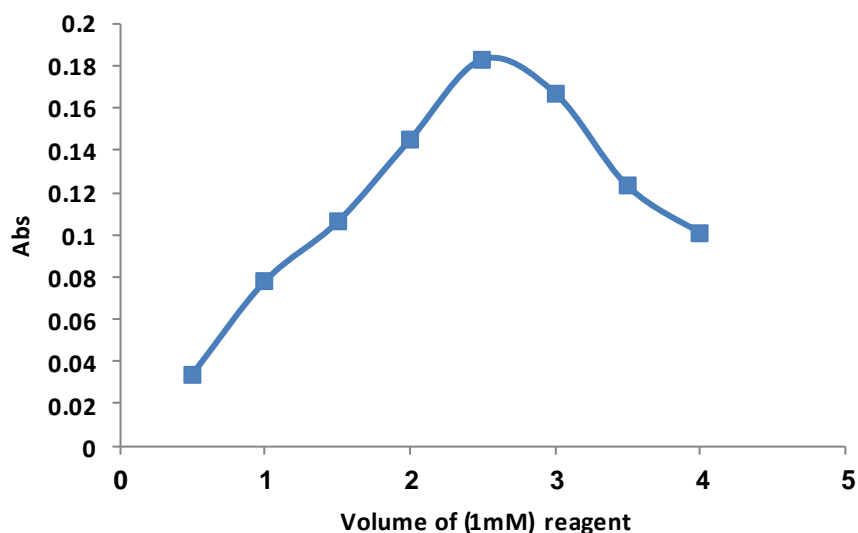


Fig.4 :- Effect of (APANN) concentration

Effect of reaction time

The colour intensity reached a maximum after the Pd (II) has been reacted immediately with APANN and became stable after three

minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least 24 hours Fig 5.

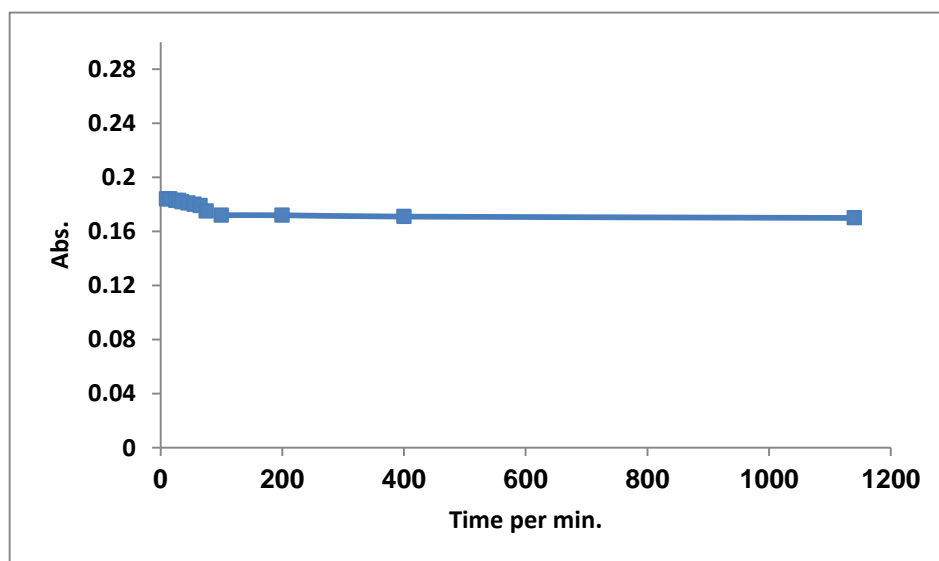


Fig.5:-Effect of time on complex of Pd[APANN]

Calibration graph

Employing the conditions described under procedure a linear calibration graph of palladium (II) is obtained which shows that Beer's

law is obeyed over the concentration range of (0.1-2.0 ppm) with correlation coefficient of 0.996 and an intercept of 0.0017.

Composition of the complex

The composition of complex was studied in the excess of reagent solution by the mole-ratio method Fig 6. A break at a 1:1 (M:L) mole

ratio suggested the formation of complex where $M = \text{Pd(II)}$ and $L = \text{APANN}$ under the given condition.

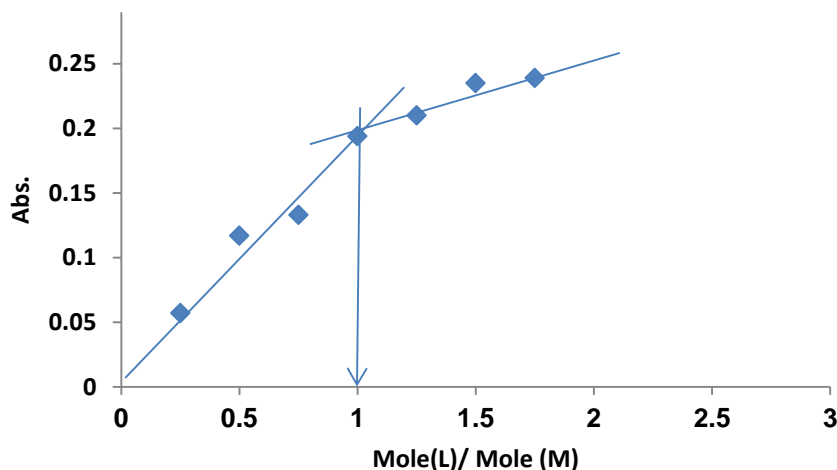


Fig 6:- mole-ratio method for Pd (II) -complex

Conductivity measurements

The solubility of the complex in dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and ethanol permitted of the molar conductivity of 1×10^{-4} M solution at

25 °C and by comparison, the electrolytic nature for complex. The low values of the molar conductance data listed in (Table 2) indicate that the complex is non electrolyte⁽¹⁴⁾.

Table 2. Conductivity values of complex

Complex	Molar conductivity, S. mole ⁻¹ .cm ² DMSO	Molar conductivity, S mole ⁻¹ . cm ² Ethanol	Molar conductivity, S mole ⁻¹ . cm ² DMF
Pd (APANN)	14.78	13.69	17.44

FT.IR of reagent and it's complex

The FT.IR of the free ligand and it's metal chelate were carried out in the (400-4000) cm⁻¹

Range. The IR bands of the (APANN) and its Pd (II) complex with their probable assignment are given in Table.3. The IR spectrum of ligand shows a broad band at 3425 cm⁻¹, which can be attributed to the OH group⁽¹¹⁾. However, the $\nu(\text{N}=\text{N})$ stretching band in the free ligand is

observed at 1535 cm⁻¹⁽¹¹⁾. This band is shifted to lower with low intensity at 1507 cm⁻¹ frequency value upon complexation suggesting chelation via the (M-N). The IR spectrum of the ligand revealed a sharp band at 1650 cm⁻¹ due to $\nu(\text{C}=\text{O})$ of pyrazole azo⁽¹¹⁾. This band is shifted to higher with low intensity at 1681 cm⁻¹ frequency value upon complexation. The bonding of oxygen to the metal ion is provided by the occurrence of

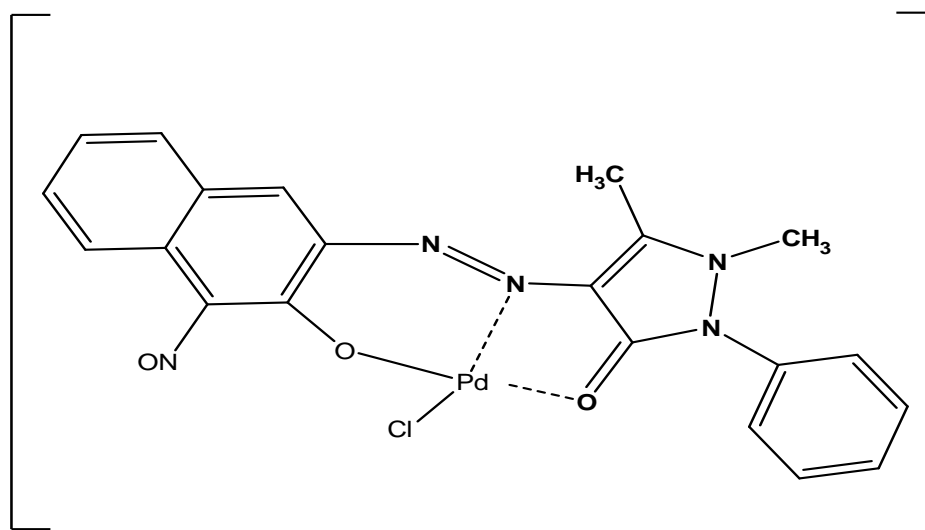
band at 457 cm^{-1} as the result of $\nu(\text{M-O})^{(14-19)}$.

Table. 3 :Selected FT.IR data of (APANN) and it's complex with Pd (II)

Compound	$\nu(\text{OH})$	$\nu(\text{C=N})$	$\nu(\text{C-H})$ arom.	$\nu(\text{N=N})$	$\nu(\text{C=C})$	$\nu(\text{C=O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
HL	3425 m	1697 s	3062 m	1535 m	1627 s	1650 s	—	—
[Pd (L)]	3409 m	-	3062 m	1507 m	1627 s	1681 s	457 w	419 w

S: sharp ; m: medium ; w: weak

On the basis of the FT.IR, stoichiometric, and elemental analysis molar conductivity data the structure of complex can be suggested as the following in Scheme .2:-



Schem.2. The suggested structural formula of Pd(II) -complex

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الخلاصة:

تم تطوير طريقة طيفية جديدة وسريعة وحساسة في تقدير الكميات الضئيلة للبلاديوم الثنائي، اعتمدت الطريقة على أساس تكوين معقد 1:1 (فلز- كاشف) مع الكاشف 3-(4-انتي بايريل آزو) -1-نايتروزو-2-نفثول (APANN)، يمتلك المعقد أعلى قمة إمتصاص عند الطول الموجي (436,5) نانوميتر ومعامل إمتصاص مولاري $10 \times 0,19$ لتر. مول⁻¹. سم⁻¹. كانت العلاقة الخطية بين الإمتصاص عند الطول الموجي الأعظم والتراكيز تتراوح بين (0.1-2) جزء في المليون.